Poly(Oxime–Ester) Vitrimers with Catalyst-Free Bond Exchange

Changfei He,[1] Shaowei Shi*[1], Dong Wang*[1], Brett A. Helms[2] and Thomas P. Russell*[1, 3, 4]

[1]Beijing Advanced Innovation Center for Soft Matter Science and Engineering & State Key Laboratory of Organic−Inorganic Composites，Beijing University of Chemical Technology, Beijing, 100029, China

[2]The Molecular Foundry, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States

[3]Polymer Science and Engineering Department, University of Massachusetts Amherst, Massachusetts 01003, United States

[4]Materials Sciences Division, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States

Supporting Information Placeholder

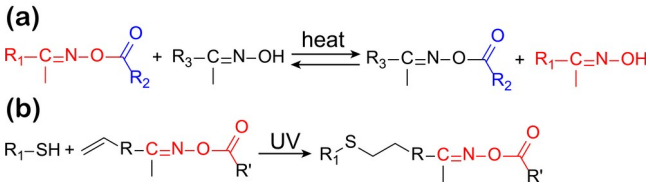
ABSTRACT: Vitrimers are network polymers that undergo associative bond exchange reactions in the condensed phase above a threshold temperature, dictated by the exchangeable bonds comprising the vitrimer. For vitrimers, chemistries reliant on poorly nucleophilic bond exchange partners (e.g., hydroxy-functionalized alkanes) or poorly electrophilic exchangeable bonds, catalysts are required to lower the threshold temperature, which is undesirable in that catalyst leaching or deactivation diminishes its influence over time and may compromise re-use. Here we show how to access catalyst-free bond exchange reactions in catalyst-dependent polyester vitrimers by obviating conventional ester bonds in favor of oxime–esters. Poly(oxime–ester) (POE) vitrimers were synthesized using thiol–ene click chemistry, affording high stretchability and malleability. POE vitrimers were readily recycled with little degradation of their initial mechanical properties, suggesting exciting opportunities for sustainable plastics.

Vitrimers are a class of thermally re-processable network polymers, which rely on associative dynamic covalent bond exchange reactions to flow, relax, and recover. Subsequent to the pioneering work of Leibler[1] and co-workers, a series of vitrimers[2] or vitrimer-like[3,4] materials have been developed by different types of dynamic covalent bonding reactions, such as transesterification,[5–10] vinylogous urethane transamidation,[11,12] transcarbamoylation,[13–15] olefin metathesis,[16] imine bond exchange,[17–19] boronic ester exchange,[20–22] alkoxysilane exchange reaction,[23–25] Diels−Alder cycloaddition,[26,27] reversible radical chemistry,[28,29] oxime−carbamate transcarbamoylation.[30] and diketoenamine exchange.[31] Dynamic transesterification reactions, however, usually rely on large amounts of catalysts, such as $Zn(OAc)_2$[1], $Sn(Oct_2)$[5], TBD[7], DBU[32], which are often toxic or have poor miscibility with vitrimer networks, which limits their applications. Moreover, the activation barrier for bond exchange reactions in transesterification reaction systems is usually high, requiring high temperatures for vitrimer reprocessing, which tends to degrade the vitrimer on repeated recycling. Developing a catalyst-free ester-based vitrimer chemistry with intrinsically low viscosities at high temperatures for processing and high viscosities at service temperature for creep resistance is desirable, but remains an outstanding challenge.

Oxime chemistry provides a promising strategy to prepare dynamic covalent polymeric materials. Oximes have a lower pK_a than aliphatic alcohols.[33] Therefore, we hypothesized that it could be feasible to carry out transesterification reactions in poly(oxime–ester) (POE) vitrimers without using an embedded catalyst. Here, we show that indeed, oxime–ester bonds (Scheme 1a) are associative dynamic covalent bonds from which to prepare POE vitrimers that require no embedded catalysts to initiate bond exchange in the solid-state. POE vitrimers were prepared using a rapid photo-initiated thio–ene click reaction (Scheme 1b). POE vitrimers, within the formulation ranges explored here, exhibited high malleability and excellent reprocessability, in that they are readily recycled with little degradation of their initial mechanical properties.

Scheme 1. (a) Transesterification of oxime–ester

bonds. (b) Incorporating oxime–ester bonds into vitrimer networks using photocuring.



To investigate the bond exchange reaction mechanism (Scheme S6) of oxime–ester bonds (Figure 1a), we synthesized small molecule oxime–ester **1** and oxime **2**, and mixed them in 1:1 stoichiometric ratio in deuterated chloroform ($CDCl_3$).The ^{1}H NMR spectrum of the mixture in Figure 1b showed that, at room temperature, for **1** and **2**, the proton signals of the methyl group near the nitrogen atom were located at 2.38 ppm and 2.26 ppm, respectively. Upon heating, two new proton signals at 2.34 ppm and 2.30 ppm appeared, giving a clear proof that the exchange reaction took place, producing target molecules **3** and **4**. This result was further confirmed by mass spectroscopy (Figure S2). The integral area of methyl proton of *a'* and *b'* increased gradually as temperature and time increased, which showed that the consumption of **1** and **2** and the formation of **3** and **4** (Figure 1b and Figure S1). The consumption of **1** was significantly influenced by temperature (Figure 1c) and the oxime transesterification rate constant was calculated to be 0.07 to 0.66 h^{-1} as temperature increased from 40 to 70 °C (Figure S1 and details can be found in SI). Arrhenius analysis of the model reaction gave an oxime transesterification activation energy (E_a) of 63.5 ± 7.8 kJ mol^{-1}, which is lower than that of conventional epoxy ester system containing catalysts (Figure 1d). [1, 5, 7] Moreover, in order to confirm that the dynamic exchange reaction mechanism is the oxime transesterification but not the imine exchange, two oxime–ester of **1** and **8** were also mixed at 1:1 stoichiometric ratio in DMSO-d_6 and were heated to 150 °C for 2 h (Figure S3). The NMR results suggest that there is no formation of **3** and **10**, indicating the imine exchange of oxime ester is negative under 150 °C.

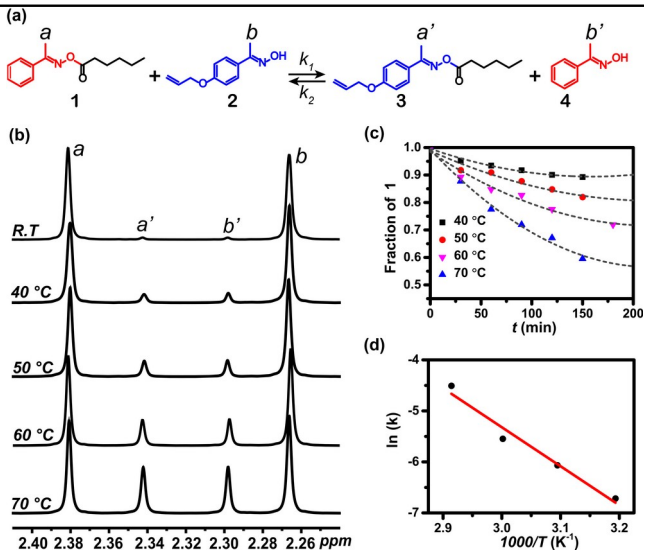


Figure 1. (a) Proposed oxime–ester exchange reaction. (b) ^{1}H NMR spectrum of the dynamic exchange reaction of oxime ester at different temperature for 120 min. (the peaks indicate methyl group near the nitrogen atom) (c) The consumption of **1** through oxime transesterification as a function of time at different temperature. (d) Arrhenius analysis and the activation energy of oxime ester exchange reaction.

After studying the dynamic nature of the reaction systems based on small molecules, POE networks using thiol–ene click chemistry were produced. Oxime–ester monomer **5** was first synthesized by the reaction between oxime **2** and adipyl chloride. Three cross-linked POE networks were constructed by photopolymerizing **2**, monomer **5**, 3,6-dioxaoctane-1,8-dithiol **6** and pentaerythritol *tetrakis*(3-mercaptopropionate) (PETMP) **7**, all with different ratios (Figure 2a, Scheme S1 and Table S1). It should be noted that the incorporation of oxime **2** provided sufficient oxime hydroxy groups for transesterification. The complete consumption of the thio group and incorporation of oxime ester components were confirmed by FTIR for all of the three cross-linked networks (Figure S4). The resultant network can then be remolded into ~1 mm thickness of film due to the facile topologic rearrangement via oxime transesterification (Figure 2b). Swelling experiments in THF at room temperature showed that all three networks were insoluble but swollen after 48 h, with a gel fraction of 98.6%, 96.8% and 92.6% for POE-a, POE-b and POE-c respectively (Table S2). By taking POE-b as an example, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) yielded a glass-transition temperature (T_g) of 7.5 °C and good thermal stability with a weight loss of 5% at 250 °C (Figure S5 and S6, Table S2). Dynamic mechanical analysis (DMA) shows that storage modulus of POE-b is 2.9 GPa in the glass state and then experience an abrupt drop in the storage modulus in the rubbery state to 4.2 MPa (Figure S7). As expect, the molecular weight between cross-links (M_c) increase from 1.7 to 4.5 kg mol^{-1} as we increase the equivalent of flexible chain (Table S2). Tensile tests

demonstrated that POE-b had a strain-at-break (ε_b) of 160 ± 22% and a stress-at-break (σ_b) of 2.2 ± 0.27 MPa, which are similar to mechanical properties of elastomers (Table S3, Figure S11).

To study the thermal reversibility of the bulk materials, two pieces of POE-b were immersed into *N*-methyl pyrrolidone (NMP) respectively, while one NMP solvent containing excess acetophenone oxime. As shown in Figure 2d, after heating the solvent to 120 °C for 24 h, the POE networks are insoluble in pure NMP, but can be completely dissolved in NMP with excess acetophenone oxime (Figure 2c), which suggests such oxime transesterification in the network is in keeping with the associative mechanism of vitrimers. On the other hand, as-synthesized linear POE was treated with 1 equivalent acetophenone oxime at 120 °C for 2 h. Gel permeation chromatography (GPC) curves shows a remarkable degradation of linear POE (Figure 2d), further indicating thermal reversibility of oxime-ester bonds via oxime transesterification, which is in good agreement with the results of small molecule models.

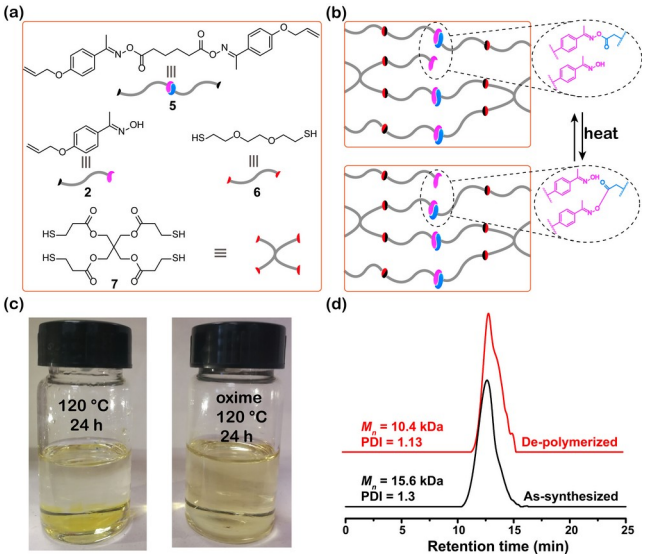


Figure 2. (a) Chemical structure of monomers for building oxime–ester network. (b) Exchange process of POE network via oxime transesterification in POEs. (c) The solubility of POE-b in NMP: swollen (left: 120 °C for 24h) and dissolved (right: 120 °C for 24 h). (d) GPC analysis of thermodynamic depolymerization of linear POE in *N,N*-dimethylformamide.

The rheological properties of as-prepared POE vitrimers were studied by stress-relaxation experiments performed using DMA. In the linear viscoelastic regime, a 3% strain was applied on the samples and stress decay was monitored as a function of time. As shown in Figure 3a and S8, a full stress-relaxation was observed at all temperatures despite the highly cross-linked chemical structures, indicating the highly malleable of POEs. The relaxation time (τ) is determined when the stress of POEs relax to 1/e of their original stress. The well-fit line of relaxation time verse temperature suggests POE networks have Arrhenius flow characteristics. Activation energies calculated from the slope of lines are in close agreement with oxime transesterification activation energy of small molecule models (Figure 3b). The result indicates that the oxime transesterification dominates the relaxation behavior in bulk materials, therefore the relaxation time or viscosity are Arrhenius. It should be noticed that with an increasing content of free oxime hydroxy group, the relaxation time decreases for POE-a, from 5102 s to 3897 s, then to 2725 s at 100 °C (Figure S9), which is another proof that the reversible reaction in the bulk materials is through oxime transesterification. Creep-recovery experiments were performed at an applied stress of 0.1 MPa and the strain was monitored. At low temperature (50 °C), the reversible exchange reaction is frozen, so the materials behave like the conventional thermosets, with no deformation and most strain recovers. While as temperature increases, oxime transesterification is activated, for example, POE-b exhibits deformation rate of 1% min^{-1} at 110 °C, and the residual strain is up to 24% (Figure 3c, Figure S10). In a word, the flow ability and malleability in bulk POEs is controlled by associative oxime transesterification.

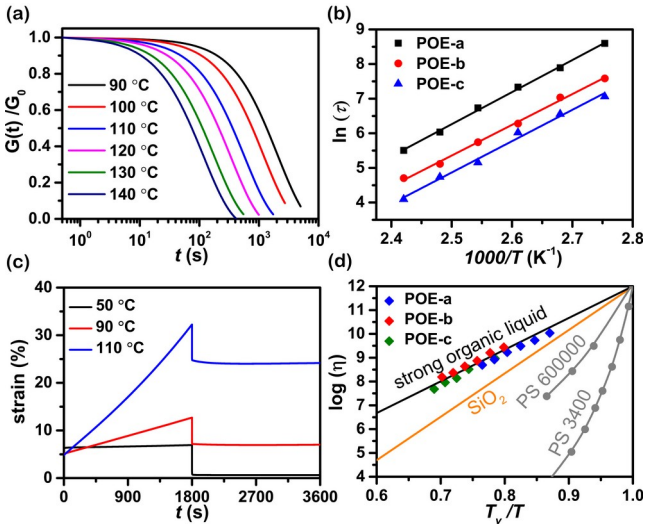


Figure 3. (a) Normalized stress-relaxation curves of POE-b at different temperature. (b) Arrhenius analysis and the activation energy of POE networks. (c) Tensile creep and recovery of POE-b with an applied stress of 0.1 MPa at different temperature. (d) Angell fragility plot showing viscosity as a function of inverse temperature normalized to T_v of polystyrene[34], silica[35] and POEs.

The topology freezing transition temperature, T_v, corresponding to the transition from the solid to the liquid state, is determined by the point when the viscosities becomes higher than 10^{12} Pa s^1. For three POE networks, T_v is in the range of 12−43 °C (Table S2), which is a little higher than their T_g, indicating POE networks are highly malleable in major rubbery plateau. The well-fit Angell fragility plot shows the viscosity of POEs follows an Arrhenius law over a very broad range temperature, which is similar to

inorganic compounds (e.g. silica[35]), rather than organic polymers (e.g. polystyrene[34]) (Figure 3d).

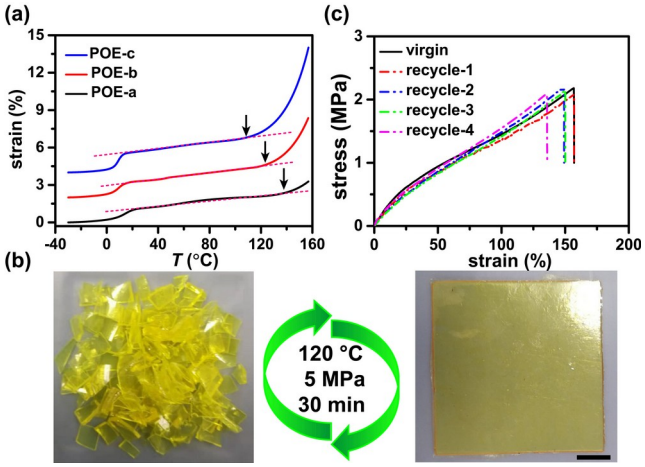


Figure 4. (a) Temperature dependence of thermal expansion of POE networks with a heating rate of 2.5 K min^{-1}. (b) Recycling POE-b from pieces to reshaped transparent film (scale bar: 1cm). (c) Stress-strain curves of POE-b and recycled POE-b.

Dilatometry experiments provide information of volume changes as a material undergo thermal transition.[1, 7] It is well-known that the thermal expansion coefficient of a polymer network without reversible chemical bonds remains constant above T_g. However, for a polymer network with reversible covalent bonds, segmental motion is triggered by the breaking and reforming of bonds. Once topological rearrangement is activated upon heating, an obvious increase in the expansion coefficient of networks is observed and the network becomes malleable. As shown in Figure 4a, a notable increase of expansion coefficient was observed at temperature of 134, 122 and 109 °C for POE-a, POE-b and POE-c respectively. The different temperatures where the POE networks become malleable is attribute to differences in the cross-link density and it provides guidance for reprocessing temperatures.

To test the reprocessability of POE vitrimers, the networks were cut into pieces and then molded into bulk materials. (Figure 4b). The reprocessed samples were characterized by DMA, DSC, FTIR and tensile testing. The mechanical properties including stress, Young's moduli and strain-at-break of the reprocessed samples are very close to those of the initial samples (Table S3 Figure S11). DMA confirmed the reprocessed sample have the same moduli at rubbery plateau (Figure S14), which indicates the density of the cross-links are constant during the remolding process. No T_g variation was observed in recycled samples (Figure S13) and no chemical change was measured by ATR-FTIR (Figure S12). In addition, welding experiments were performed by cutting a rectangle bar (1mm (T) × 6mm (W) × 30mm (L)) into two pieces and then placing them in contact at 120 °C for 10 min. Optical microscopy images show that the cracks almost disappear and the welded sample can be loaded up to 0.2 kg (Figure S15).

In summary, we have designed and synthesized a new catalyst-free POE vitrimers by using photo-initiated "thio–ene" reactions at room temperature. The UV-polymerization of vitrimers shows a great advantage for vitrimer manufacturing, which sets up a whole range of processing techniques access to a networked architecture facile and efficient. Similar to thermosets, POE networks are insoluble in normal organic solvents with good structural stability. However, at high temperature, owing to the oxime transesterification, POE networks exhibit excellent malleability and reprocessability. This new dynamic network was found to be easily reprocessed and recycled numerous times without degradation of the chemical and physical properties. Due to the highly effective and efficient synthesis, and tuneable monomers, POE vitrimes afford networks with a range of tuneable properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Experimental details and characterization data

AUTHOR INFORMATION

Corresponding Author

*E-mail: shisw@mail.buct.edu.cn

*E-mail: dwang@mail.buct.edu.cn

*E-mail: russell@mail.pse.umass.edu

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by National Natural Science Foundation of China (51673016) and Grant No. 2194083 of Beijing Natural Science Foundation. B.A.H. acknowledges support from the Molecular Foundry, which is supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

REFERENCES

(1) Montarnal, D.; Capelot, M.; Tournilhac, F.; Leibler, L. Silica-like malleable materials from permanent organic networks. *Science* **2011**, *334*, 965-968.
(2) Capelot, M.; Montarnal, D.; Tournilhac, F.; Leibler, L. Metal-catalyzed transesterification for healing and assembling of thermosets. *J. Am. Chem. Soc.* **2012**, *134*, 7664-7667.
(3) Garcia, F.; Smulders, M. M. Dynamic covalent polymers. *J. Polym. Sci. A: Polym. Chem.* **2016**, *54* (22), 3551-3577.
(4) Bowman, C. N.; Kloxin, C. Covalent adaptable networks: reversible bond structures incorporated in

polymer networks. *J. Angew. Chem. Int. Ed.* **2012**, 51, 4272−4.
(5) Brutman, J.; Delgado, A.; Hillmyer, M. Polylactide vitrimers. *ACS Macro Lett.* **2014**, *3,* 607-610.
(6) Altuna, F. I.; Pettarin, V.; Williams, R. J. J. Self-healable polymer networks based on the cross-linking of epoxidised soybean oil by an aqueous citric acid solution. *Green Chem.* **2013**, *15, 3360-3366*.
(7) Pei, Z.; Yang, Y.; Chen, Q.; Terentjev, E. M.; Wei, Y.; Ji, Y. Mouldable liquid-crystalline elastomer actuators with exchangeable covalent bonds. *Nat. Mater.* **2014**, *13*, 36-41.
(8) Zhou, Y.; Goossens, J. P.; Sijbesma, R.; Heuts, J. A. Poly (butylene terephthalate)/glycerol-based vitrimers via solid-state polymerization. *Macromolecules* **2017**, *50*, 6742-6751.
(9) Han, J.; Liu, T.; Hao, C.; Zhang, S.; Guo, B.; Zhang, J. A Catalyst-Free Epoxy Vitrimer System Based on Multifunctional Hyperbranched Polymer. *Macromolecules* **2018**, *51*, 6789-6799.
(10) Ube, T.; Kawasaki, K.; Ikeda, T. Photomobile liquid-crystalline elastomers with rearrangeable networks. *Adv. Mater.* **2016**, *28*, 8212-8217.
(11) Denissen, W.; Rivero, G.; Nicolaÿ, R.; Leibler, R.; Winne, J. M.; Du Prez, F. E. Vinylogous urethane vitrimers. *Adv. Func. Mater.* **2015**, *25*, 2451-2457.
(12) Guerre. M.; Taplan. C.; Nicolaÿ.R.; Winne. J. M.; Du Prez. F. E. Fluorinated vitrimer elastomers with a dual temperature response. *J. Am. Chem. Soc*., **2018**, 140, 13272–13284
(13) Fortman, D.; Brutman, J.; Cramer, C.; Hillmyer, M. Mechanically activated, catalyst-free polyhydroxyurethane vitrimers. *J. Am. Chem. Soc.* **2015**, *137*, 14019-14012.
(14) Zheng, N.; Fang, Z.; Zou, W.; Zhao, Q.; Xie, T. Thermoset shape-memory polyurethane with intrinsic plasticity enabled by transcarbamoylation. *Angew. Chem. Int. Ed.* **2016**, 55, 1 – 6.
(15) Chen, X.; Li, L; Jin, K.; Torkelson, J. Reprocessable polyhydroxyurethane networks exhibiting full property recovery and concurrent associative and dissociative dynamic chemistry via transcarbamoylation and reversible cyclic carbonate aminolysis. *Polym. Chem.* **2017**, *8*, 6349-6355.
(16) Capelot, M.; Montarnal, D.; Tournilhac, F.; Leibler, L. Metal-catalyzed transesterification for healing and assembling of thermosets. *J. Am. Chem. Soc.* **2012**, *134*, 7664-7667.
(17) Chao, A.; Negulescu, I.; Zhang, D. Dynamic covalent polymer networks based on degenerative imine bond exchange: tuning the malleability and self-healing properties by solvent. *Macromolecules* **2016**, *49*, 6277-6284.
(18) Taynton, P.; Yu, K.; Shoemaker, R. K.; Jin, Y.; Qi, H. J.; Zhang, W. Heat-or Water-Driven Malleability in a Highly Recyclable Covalent Network Polymer. *Adv. Mater.* **2014**, *26*, 3938-3942.
(19) Taynton, P.; Ni, H.; Zhu, C.; Yu, K.; Loob, S.; Jin, Y.; Qi, H. J.; Zhang, W. Repairable woven carbon fiber composites with full recyclability enabled by malleable polyimine networks. *Adv. Mater.***2016**, 49, 6277-6284.
(20) Rottger, M.; Domenech T.; van der Weegen, R.; Breuillac A.; Nicolay, R.; Leibler, L. High-performance vitrimers from commodity thermoplastics through dioxaborolane metathesis. *Science* **2017**, *356*, 62-65.
(21) Ogedn, W; Guan, Z. Recyclable, strong, and highly malleable thermosets based on boroxine networks. *J. Am. Chem. Soc.* **2018**, *140*, 6217-6220.
(22) Cromwell, R.; Chung, J.; Guan, Z. Malleable and self-healing covalent polymer networks through tunable dynamic boronic ester bonds. *J. Am. Chem. Soc.* **2015**, *137*, 6492-6495.
(23) Zheng, P.; McCarthy, T. J. A surprise from 1954: siloxane equilibration is a simple, robust, and obvious polymer self-healing mechanism. *J. Am. Chem. Soc.***2012**, 134, 2024-2027.
(24) Nishimura, Y.; Chung, J.; Muradyan, H.; Guan, Z. Silyl ether as a robust and thermally stable dynamic covalent motif for malleable polymer design. *J. Am. Chem. Soc.*2017, 139, 14881–14884.
(25) Stukenbroeker, T.; Wang, W. Winne, J. Du Prez, F.; Nicolay, R.; Leibler, L. Polydimethylsiloxane quenchable vitrimers. *Polym. Chem.* 2017, 8, 6590–6359.
(26) Chen, X.; Dam, M. A.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. A. A thermally re-mendable cross-linked polymeric material. *Science* **2002**, 295, 1698−1702.
(27) Zhang, G.; Zhao, Q.; Yang, L.; Zou, W.; Xi, X.; Xie, T. Exploring dynamic equilibrium of Diels–Alder reaction for solid state plasticity in remoldable shape memory polymer network. *ACS Macro Lett.* **2016**, 5 (7), 805-808.
(28) Amamoto, Y.; Otsuka, H.; Takahara, A.; Matyjaszewski, K. *Adv. Mater.* **2012**, 24, 3975−3980.
(29) Zhang, Z.; Rong. M.; Zhang. M. Self-healing of covalently cross-linked polymers by reshuffling thiuram disulfide moieties in air under visible light. *Adv. Funct. Mater.* **2018**, 24, 1706050.
(30) Liu. W.; Zhang. C.; Zhang. H.; Zhao. N.; Yu. Z.; Xu. J. Oxime-based and catalyst-free dynamic covalent polyurethanes. *J. Am. Chem. Soc.* **2017**, 139, 8678-8684.
(31) Christensen, P. R.; Scheuermann, A. M.; Loeffler, K. E.; Helms, B. A. Closed-loop recycling of plastics enabled by dynamic covalent diketoenamine bonds. *Nat. Chem.* **2019**, 11, 442–448.
(32) Song, H.; Fang, Z.; Jin, B.; Pan, P.; Zhao, Q.; Xie, T. Synergetic chemical and physical programming for reversible shape memory effect in a dynamic covalent network with two crystalline phases. *ACS Macro Lett.* **2019**, 8, 682-686.
(33) Pearse, G.A., Jr.; Pflaum, R.T. Interaction of Metal Ions with Amidoximes. *J. Am. Chem. Soc.* **1959**, 81, 6505.
(34) Plazek, D. J.; O'Rourke, V. M. Viscoelastic behavior of low molecular weight polystyrene. *J. Polym. Sci. A-2 Polym. Phys.* **1971**, 9, 209.
(35) Urbain, G.; Bottinga, Y.; Richet, P. Geochim. Viscosity of liquid silica, silicates and alumino-silicates. *Cosmochim. Acta* **1982**, 46, 1061.

Table of Contents